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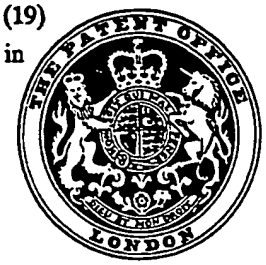

(54) IMPROVED PHOTOPOLYMERIZABLE COMPOSITIONS FOR THE PRODUCTION OF PRINTING PLATES AND RELIEF PLATES

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to improved photopolymerizable compositions which may be used for the production of printing plates and relief plates which comprise a mixture of at least one photopolymerizable non-polymeric material, a photoinitiator and a polymeric binder.

Photopolymerizable compositions for the production of printing plates have frequently been described, it being possible to employ both fluid and solid compositions. For example, German Laid-Open Application DOS 20 40 390 discloses fluid resin compositions based on mixtures of 5 to 55% by weight of unsaturated monomers, such as acrylic or allyl compounds, and 95 to 45% by weight of an unsaturated polyester, which contain conventional amounts of a photoinitiator and a thermal polymerization inhibitor, and are used to produce relief printing plates by imagewise exposure of layers thereof and subsequent washout of the unexposed areas with a developer solution. When printing plates having relief heights of from about 0.5 to 1mm, which are the ones usually employed in the graphic industry, are produced with these conventional compositions for instance, they usually do not exhibit a sharp relief image and often have side walls which are not steep enough.

It is known that improved relief printing plates can be obtained by techniques of exposure of the photopolymer plates through the image-bearing negative; employing multi-layer photopolymer plates; or arranging other layers beneath the photopolymer layer, which layers influence the sidewall structure of the relief. However, these methods are complicated and expensive.

The present invention seeks to provide photopolymerizable compositions which are able to give relief plates having an improved relief image, in particular a better depth of shadow wells, in the conventional method of producing such plates.

We have found that good results may be obtained by the incorporation of 9-nitroanthracene into the photopolymerizable compositions.

According to the present invention there is provided a photopolymerizable composition for the production of printing plates and relief plates comprising a photoinitiator, one or more photopolymerizable non-polymeric materials, a polymeric binder and 9-nitroanthracene.

Preferably, the non-polymeric material is a low molecular weight compound having at least one olefinically unsaturated photopolymerizable double bond, the polymeric binder is an organic polymeric binder that is compatible with said compound, and the composition contains uniformly dispersed therein, from 0.001 to 2% by weight, based on the whole composition, of 9-nitroanthracene.

To better assess the quality of the image in different sections of the relief of one and the

same plate, it is advantageous to measure the depth of shadow wells in halftone areas produced with screens of different ruling and tone value, and for negative dots, having a diameter of 400 µm, in a solid area. Figure 1 of the accompanying drawings shows how, after exposure of a layer L of a photopolymerizable composition with actinic light through a negative N and development by washing out the non-polymerized areas of the layer L with a developer solution a relief having a relief height h_R and a shadow well depth t_z in a halftone area of 50% tone value, this depth being referred to hereinafter as "$t_z(50)$", is produced. The same is shown in Figure 2 of the drawings for an opaque dot (in negative N) having a diameter of 0.4 mm in a clear area which is large in relation thereto, here and hereinafter referred to as "negative dot", the shadow dot depth being referred to hereinafter as $t_z(nP400)$. As the Examples described below show, a considerable improvement in the shadow well depth and hence in the structure of the relief can be achieved with a composition within the invention.

The polymeric binders used for the photopolymerizable compositions according to the invention may be those conventionally used for this purpose. In practice, the binder must be compatible with the co-used monomers and - which is evident to the skilled artisan - be soluble or dispersible in the developer solutions employed, to enable the unexposed and hence non-crosslinked areas of layer L of the photopolymerizable composition, after imagewise exposure thereof, to be washed out. Specific examples of suitable polymeric saturated or unsaturated binders are linear polyamides and particularly alcohol-soluble copolyamides such as are described in French Patent 1,520,856, cellulose derivatives, particularly cellulose derivatives which can be washed out with aqueous alkaline solutions, vinyl alcohol polymers and homopolymers and copolymers of vinyl esters of aliphatic monocarboxylic acids of 1 to 4 carbon atoms, e.g. of vinyl acetates, having varying degrees of saponification, polyurethanes, polyether-urethanes and polyester-urethanes, particularly polyester resins, especially those disclosed in German Laid-Open Application (DOS) 20 40 390. Of the linear or branched polyesters produced by reaction of unsaturated and/or saturated dibasic and/or higher polybasic carboxylic acids with dihydric and/or higher polyhydric alcohols, those which have a relatively high acid number and especially an acid number of from 75 to 160 are preferred because they result in the compositions being readily dispersible or soluble in aqueous alkaline developer solutions. With regard to the composition and production of unsaturated polyester resins reference is made to the existing literature, e.g. H.V. Boenig, Unsaturated Polyesters, Structure and Properties, Amsterdam, 1964. The content of polymeric binder in the composition is generally from about 45 to 90% by weight and especially from 45 to 65% by weight, based on the amount of polymer and photopolymerizable monomers.

The photopolymerizable non-polymeric materials may be monomeric, low molecular weight compounds having at least one olefinically unsaturated photopolymerizable double bond conventionally used for photopolymer printing plates. In practice, such monomers must form compatible mixtures with the particular polymeric binder employed and have a boiling point of more than 100°C at atmospheric pressure. Monomers having two or more olefinically unsaturated photopolymerizable double bonds are preferred; these may be used alone or in admixture with monomers having only one olefinically unsaturated photopolymerizable double bond, the content of the latter being generally from 5 to 50% by weight and preferably from 5 to 30% by weight of the total amount of monomers. The type of monomers used depends substantially on the type of co-used polymeric binder. Particularly suitable in the case of mixtures with unsaturated polyester resins are allyl compounds containing two or more double bonds, such as dialkyl maleate, allyl acrylate, diallyl phthalate, trimellitic acid diallyl and triallyl esters, and ethylene glycol bisallyl carbonate, as well as diacrylates, polyacrylates, dimethacrylates and polymethacrylates such as may be obtained by esterification of diols or polyols with acrylic acid and methacrylic acid respectively, e.g. the diacrylates, triacrylates, dimethacrylates and trimethacrylates of ethylene glycol, diethylene glycol, triethylene glycol and polyethylene glycol having a molecular weight of up to 500, 1,2-propanediol, 1,3-propanediol, neopentyl glycol (2,2-dimethylpropanediol), 1,4-butanediol, 1,1,1-trimethylolpropane, glycerol and pentaerythritol; also very suitable are the monoacrylates and monomethacrylates of such diols and polyols, e.g. ethylene glycol monoacrylate, diethylene glycol monoacrylate, triethylene glycol monoacrylate and tetraethylene glycol monoacrylate, monomers having two or more olefinically unsaturated bonds which contain urethane groups and/or amide groups, such as the low molecular weight compounds produced from aliphatic diols of the aforementioned type, organic diisocyanates and hydroxyalkyl acrylates and methacrylates. Further examples are acrylic acid, methacrylic acid and derivatives thereof, such as acrylamide, methacrylamide, N-hydroxymethyl acrylamide or methacrylamide, and acrylates or methacrylates of monoalcohols of 1 to 6 carbon atoms. Mixtures of allyl monomers with diacrylates or polyacrylates are very suitable. When compositions containing a

polyamide as the polymeric binder are employed, of the said types of monomer not only are diacrylates and polyacrylates particularly suitable, but also those which contain amide and/or urethane groups in addition to the double bonds, such as derivatives of acrylamides, e.g. the reaction products of 2 moles of N-(hydroxymethyl)acrylamide or N-(hydroxymethyl)methacrylamide and 1 mole of an aliphatic diol, such as ethylene glycol, xylylene bisacrylamide and alkylene bisacrylamides of 1 to 8 carbon atoms in the alkylene radical. Water-soluble monomers, e.g. hydroxyethyl acrylate or methacrylate, and monoacrylates, diacrylates, monomethacrylates or dimethacrylates of polyethylene glycols having a molecular weight of 200 to 500 are particularly suitable for the production of printing plates which can be developed with aqueous alkaline solutions and contain polyvinyl alcohol as polymeric binder.

The amount of monomer or monomer mixture is generally from 10 to 55% by weight and particularly from 35 to 55% by weight, based on the amount of polymer and photopolymerizable monomers, and is determined by, inter alia, the compatibility of the monomer or monomer mixture and the desired hardness of the resulting relief plate.

The photopolymerizable compositions preferably contain, as is customary in the art, from 0.01 to 10%, particularly from 0.01 to 3%, by weight, based on the composition, of photoinitiators; virtually all compounds which upon exposure to actinic light are capable of forming radicals which initiate polymerization are suitable as photoinitiators. Examples of suitable compounds are acyloins, acyloin ethers, aromatic diketones and derivatives thereof, polynuclear quinones, acridine derivatives and phenazine derivatives. Very suitable are benzoin and α-hydroxymethylbenzoin and their alkyl ethers of 1 to 8 carbon atoms, such as benzoin isopropyl ether, α-hydroxymethylbenzoin methyl ether and benzoin methyl ether, benzil monoketals, such as benzil monodimethyl ketal, benzil monomethyl ethyl ketal, benzil monomethyl benzyl ketal and benzil mononeopentyl ketal.

It is advantageous to add to the photopolymerizable compositions conventional thermal polymerization inhibitors, e.g. hydroquinone, p-methoxyphenol, dinitrobenzene, p-quinone, methylene blue, β-naphthol, N-nitrosamines, such as nitrosodiphenylamine, phenothiazine, phosphorous acid esters, such as triphenyl phosphite, and the salts, particularly the alkali metal and aluminum salts, of N-nitrosocyclohexylhydroxylamine.

Compositions within the invention may also contain other conventional additives, e.g. plasticizers, saturated low molecular weight compounds having amide groups, and waxes.

Processing of the photopolymerizable compositions into photopolymer printing plates having the composition as the relief-forming layer may be effected in the conventional manner and is dependent on the type of mixture and on whether the composition is liquid or solid. Relief plates are produced from the blank material in the conventional manner by imagewise exposure with actinic light from light sources whose emission maxima are in the absorption range of the photoinitiators, generally in the range from 300 to 400 nm, or which emit a sufficient proportion of light of this wavelength range, e.g. low-pressure, medium-pressure and high-pressure mercury vapor lamps, and superactinic fluorescent tubes. After imagewise exposure, the unexposed areas of the layer are removed mechanically or washed out with developer solution in the conventional manner, and the resulting relief plate is dried. In some cases it may be advantageous to after-expose the entire relief.

Liquid photopolymerizable compositions which have proved highly suitable are mixtures of:-

(a) 45 to 75% by weight of an unsaturated polyester having an acid number of 100 to 150,
(b) 15 to 25%, particularly 10 to 20%, by weight of a monomer having two carbon-carbon double bonds and containing at least one allyl group,
(c) 5 to 25% by weight of a monomer having at least one acrylate or methacrylate group,
(d) 1 to 10% by weight of a saturated or unsaturated low molecular weight compound having at least one amide group,
(e) 0.2 to 4% by weight of a photoinitiator,
(f) 0.003 to 1% by weight of a thermal polymerization inhibitor, and
(g) 0.001 to 0.5%, particularly 0.004 to 0.02%, by weight of 9-nitroanthracene.

The parts and percentages given in the following Examples and comparative Experiments are by weight, unless stated otherwise. Parts by weights bear the same relation to parts by volume as the kilogram to the liter.

Example 1

1 part of a mixture of about 45% of tetraethylene glycol diacrylate, 35% of diallyl phthalate, 17% of acrylamide, 2% of benzoin isopropyl ether and 0.1% of triphenyl phosphite is stirred into 1.6 parts of an unsaturated polyester condensed to an acid number of 148 and prepared from 5 moles of fumaric acid, 3 moles of adipic acid, 2 moles of trimellitic anhydride and 9 moles of diethylene glycol. 75 ppm, based on the whole mixture,

of 9-nitroanthracene is mixed into the mixture.

Relief printing plates are produced from the resulting composition in the conventional manner:-

The liquid composition is cast in a layer of steel sheets, coated with adhesive, serving as supports, and the applied layers are brought to a thickness of 800 µm with a doctor and then covered with pieces of 9 µm thick transparent polyester film while avoiding the inclusion of air. The layers of liquid resin are then exposed imagewise through negatives, placed on the polyester films, with a conventional medium-pressure UV lamp. The negatives and polyester films are removed and the unexposed areas of the layers are washed out with a 0.5% strength aqueous sodium bicarbonate solution. The resulting relief plates are dried and after-exposed for 2 minutes.

Evaluation of the relief images obtained shows that the shoulders are non-tacky and sharply defined, the shadow well depths in a halftone area of 50% tone value ($t_z(50)$) and for a negative dot ($t_z(nP400)$) being 130µm and 285 µm respectively.

Example 2

1.2 parts of an unsaturated polyester having an acid number of 135 and prepared from 8 moles of fumaric acid, 2 moles of trimellitic anhydride and 9 moles of diethylene glycol is mixed with 1 part of a mixture of 43% of diallyl phthalate, 43% of tetraethylene glycol diacrylate, 12% of acrylamide, 0.2% of hydroquinone and 2% of benzoin isopropyl ether. 60 ppm, based on the whole mixture, of 9-nitroanthracene are then added. Printing plates and relief plates are produced with the resulting composition, as described in Example 1. Evaluation of the relief images shows that the shadow well depths are advantageous and that the shoulders exhibit a favorable shape (cf. Table 1).

Comparative Experiment A

The procedure of Example 1 is followed exactly, except that no 9-nitroanthracene is added. Evaluation of the relief image shows that the shadow well depths $t_z(50)$ and $t_z(nP400)$ are unsatisfactory and the shoulder shape is unfavorable (cf. Table 1).

Table 1

Evaluation of the relief images obtained according to Example 2 and Comparative Experiment A.

	Example 2	Comparative Experiment A
Shadow well depth in a halftone area of 50% tone value $t_z(50)$	115 µm	35 µm
Shadow well depth for a negative dot 0.4 mm in diameter $t_z(nP400)$	240 µm	37 µm
Shoulders	non-tacky, sharply defined	tacky very poorly defined

WHAT WE CLAIM IS:-

1. A photopolymerizable composition for the production of printing plates and relief plates, comprising a photoinitiator, one or more photopolymerizable non-polymeric materials, a polymeric binder and 9-nitroanthracene.

2. A composition as claimed in claim 1 wherein the photopolymerizable non-polymeric material is a low molecular weight compound having at least one olefinically unsaturated photopolymerizable double bond, the polymeric binder is an organic polymeric binder compatible with said compound, and the composition contains, uniformly dispersed therein, from 0.001 to 2% by weight of 9-nitroanthracene.

3. A composition as claimed in claim 1 or 2 wherein the non-polymeric material is a monomer having two or more olefinically unsaturated photopolymerizable double bonds or a mixture thereof with a monomer having one olefinically unsaturated photopolymerizable double bond only.

4. A composition as claimed in claim 3 wherein the non-polymeric material is a mixture of a monomer having two or more olefinically unsaturated photopolymerizable double bonds with from 5% to 30% by weight of the mixture of a monomer having one olefinically unsaturated photopolymerizable double bond only.

5. A composition as claimed in any preceding claim wherein the non-polymeric material

is substantially as hereinbefore described in Example 1 or Example 2.

6. A composition as claimed in any preceding claim wherein the polymeric binder is an alcohol-soluble copolyamide, a cellulose derivative which can be washed out with an aqueous alkaline solution, a vinyl alcohol polymer, a homopolymer or copolymer of a vinyl ester of an aliphatic monocarboxylic acid of 1 to 4 carbon atoms, a polyurethane, a polyether-urethane, a polyester-urethane or a polyester resin.

7. A composition as claimed in any preceding claim wherein the non-polymeric material and the polymeric binder form a mixture consisting of 35% to 55% by weight of the non-polymeric material and from 45% to 65% by weight of the polymeric binder.

8. A composition as claimed in any preceding claim wherein the 9-nitroanthracene is present in an amount of from 0.001% to 0.5% by weight of the composition.

9. A composition as claimed in any preceding claim and comprising the following components in the following amounts based on the components in aggregate:-

(a) 45 to 75% by weight of an unsaturated polyester having an acid number of 100 to 150,

(b) 15 to 25% by weight of a monomer having two carbon-carbon double bonds and containing at least one allyl group,

(c) 5 to 25% by weight of a monomer having at least one acrylate or methacrylate group,

(d) 1 to 10% by weight of a saturated or unsaturated low molecular weight compound having at least one amide group,

(e) 0.2 to 4% by weight of a photoinitiator,

(f) 0.003 to 1% by weight of a thermal polymerization inhibitor, and

(g) 0.001 to 0.5% by weight of 9-nitroanthracene.

10. A composition as claimed in claim 9 wherein (b) consists of from 10% to 20%, by weight of the specified components in aggregate, of the specified monomer.

11. A composition as claimed in claim 9 or claim 10 wherein the 9-nitroanthracene is present in an amount of from 0.004 to 0.02% by weight of the specified components in aggregate.

12. A composition as claimed in claim 1 and substantially as described in either of the foregoing Examples 1 and 2.

13. A presensitized plate wherein there is provided a layer of a composition as claimed in any preceding claim.

14. A printed plate made from a presensitized plate as claimed in claim 13.

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1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

FIG.1

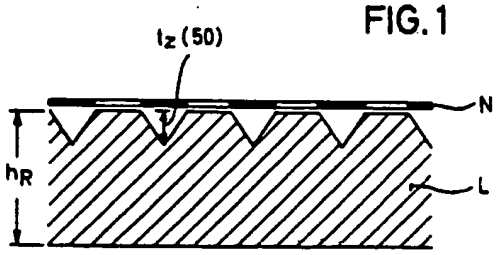

FIG.2